

Process for activation and derivatisation of cellulose

5 The present invention relates to an activation process for cellulose and a process for derivatisation of the activated cellulose and the cellulose derivatives obtained therefrom. The products produced in accordance with this process are characterised by advantageous properties, such as, for example, improved solubilities.

10 The accessibility and reactivity of cellulose is known to be influenced by its super-molecular structure. This is characterised by the presence of zones of different degrees of crystallisation, fibrillar crystallites, and the number, size and availability of internal surfaces. Cellulose is insoluble in conventional solvents such as water, dilute acids and alkaline solutions, and also in commercially available organic solvents. Derivatisation in these solvents therefore proceeds, at least at the beginning
15 of the reaction, under heterogeneous conditions. However, initially, the cellulose must be activated in an appropriate manner in order to increase the accessibility and reactivity of the hydroxyl groups in the cellulose.

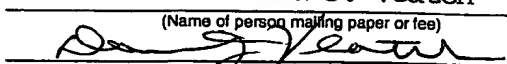
20 Known methods for activating cellulose are all directed towards an opening or expansion of the (internal) surfaces, splitting fibrillar aggregates, destroying crystalline regions and altering crystal sizes and crystal modifications. An activating effect on the subsequent reaction of cellulose is achieved, for example, by grinding, irradiation with electrons (DE 2,941,624, microwaves or γ -rays, hydrolysis, oxidation, thermal treatment, freeze-drying or treatment with substances with a swelling action (alkaline hydroxides, amines and amine complexes, ammonia
25 (EP 0,108,991), aqueous solutions of inorganic acids and salts) (Summary in Hans A. Krässig, *Cellulose-Structure, Accessibility and Reactivity*, Polymer Monographs Vol. 11, Gordon and Breach Science Publishers S.A., pages 215-277, 1993).

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In the case of the technical production of cellulose ethers, which is at present carried out exclusively under heterogeneous reaction conditions, the cellulose is generally activated by means of a preliminary treatment with concentrated alkaline solutions. The disadvantages of this approach to processing are as follows:

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1. even in the case of reactions which require only catalytic quantities of base (e.g. hydroxyl alkylation, sulfo-ethylation or cyano-ethylation), high concentrations of alkaline hydroxides are required to swell and activate the cellulose,

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2. as a result of the large quantities of alkali, a breakdown of the cellulose chain and a high salt load is unavoidable when the alkaline solution used is neutralised.

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3. complete solubility of high-viscosity cellulose ethers with low degrees of substitution cannot be achieved, and

4. distribution of the substituents introduced along and between the cellulose chains is not even.

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As an activating preliminary treatment, in which the native superstructures of the cellulose are destroyed and their crystallinity reduced, the state of the art also suggests the dissolution of the cellulose in appropriate, non-derivatising solvent systems and subsequent precipitation. The solvent systems used in this context were mixtures of sulfur dioxide/dimethylamine/dimethylsulfoxide (A. Isogai, A. Ishizu, J. Nakano, J. Appl. Polymer Sci. 31, pages 341-352, 1986), mixtures of N,N-dimethylacetamide/lithium chloride (JP 59,038,203) and dimethyl sulfoxide/paraformaldehyde (SU 3,453,670).

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These cellulose solvent systems have so far not been useful on a technical scale because of their limited dissolving power, particularly in respect of high-molecular-weight celluloses, and the difficult, and in some cases expensive, recovery of the reagents involved.

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A further class of cellulose solvents is provided by the tertiary aminoxides. It is known from US-PS 2,179,181 that cellulose is dissolved without derivatisation by certain tertiary aminoxides and that cellulose shaped bodies, e.g. fibres can be obtained by precipitation. As a cellulose solvent for the production of fibres and films, N-methyl morpholine-N-oxide-monohydrate (NMMNO-MH) has recently attracted commercial interest (US-PS 3,447,956; US-PS 4,196,282; EP 453,610; WO 95/11,261).

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Starting from the disadvantages of the known processes for derivatisation of cellulose described, the object of the present invention was to develop a process for the activation and optionally the subsequent derivatisation of cellulose, which is characterised by reduced quantities of activation and derivatisation reagents and which allows the commercial presentation of products with improved solubility properties (lower proportion of gel and fibre, very clear solution).

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The present invention therefore relates to a process for activation of cellulose comprising the following steps:

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- a) dissolution of cellulose in a water-containing, tertiary aminoxide with the optional addition of at least one appropriate stabiliser,
- b) coagulation of the dissolved cellulose by the addition of an appropriate precipitating agent and
- c) optional alkalisation of the amorphous cellulose obtained from step b).

The following are preferably used as cellulose starting materials for the process in accordance with the invention: chemical celluloses, cotton-linters, coniferous wood sulfite, coniferous wood sulfate and/or hardwood celluloses of extremely diverse level of polymerisation.

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Aminoxides selected from the group N-methyl morpholine-N-oxide (NMMNO), N-methyl-piperidine-N-oxide, N-methyl-pyrrolidine-N-oxide, N,N-dimethylcyclohexylamine-N-oxide, N,N-dimethyl-ethanolamine-N-oxide and triethylamine-N-oxide, and water (e.g. NMMNO-MH) or mixtures of water and dipolar-aprotic compounds such as in particular dimethyl sulfoxide, N-methyl pyrrolidone, dimethyl acetamide or dimethyl formamide are preferably used as the water-containing tertiary aminoxide.

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The cellulose solutions are prepared in a known manner (US-PS 4,145,532; US-PS 4,196,282; EP 452, 610; WO 95/11261) by dissolving the cellulose in a melt of NMMNO-MH at temperatures of 85 to 115°C. The cellulose material is generally stirred into an aqueous solution of NMMNO at room temperature and water is distilled off under vacuum at 85 to 115°C. In dependence upon the level of polymerisation, the concentration of cellulose is from 2 to 20%, preferably 3 to 15%.

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In order to minimise a breakdown of the cellulose during the dissolution process, at least one stabiliser is advantageously used. The stabilisers described in EP-A-047,929 are suitable, particularly gallic acid propyl ester. The preferred quantity of stabiliser is 1 wt.%, relative to the quantity of cellulose.

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The water-containing aminoxides may contain small quantities of compounds acting as bases such as tertiary amines and/or alkaline hydroxides.

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Precipitating agents suitable for the coagulation of the dissolved cellulose are in particular organic solvents such as ether, particularly dimethyl ether, ketones,

5 particularly acetone, alcohols preferably with 1-6 carbon atoms, particularly methanol, ethanol, 2-propanol or 2-methyl-2-propanol, and acetonitrile or mixtures of these solvents. The organic solvents may contain small quantities of compounds acting as bases such as tertiary amines and/or alkali hydroxides and/or quaternary ammonium bases.

10 The precipitating agent can be added to the cellulose solution both continuously and also in stages, and is advantageously also used for washing out any residual quantities of aminoxide in the precipitated cellulose.

The activation process according to the invention exhibits the following advantages by comparison with known processes with dissolution activation:

- 15 - no influence of residual lignin on the solubility of the cellulose in the pre-activation stage
- simple process design, preparation and processing of the solvent
- 20 - lower costs, simple and complete recovery of the activation reagents
- simpler removal of the activation agents from the activated cellulose (no salts)
- no environmental pollution, possibility of an enclosed solvent circuit
- 25 - higher dissolving power also for celluloses with high molecular weight
- preliminary swelling (water, water vapour, liquid ammonia), followed by a subsequent replacement of the solvent is not required for preparation of the solvent.

The activation process according to the invention leads to amorphous cellulose with increased reactivity and also allows a direct derivatisation without preceding alkalisation stage (e.g. esterification to form cellulose acetate, -nitrate or -lactate, and/or conversion with isocyanates). whereby improved yields of cellulose derivatives with improved solubility are achieved.

The present invention therefore also relates to a process for derivatisation of cellulose containing the steps:

- a) dissolution of cellulose in a water-containing, tertiary aminoxide, with the optional addition of appropriate stabilisers.
- b) coagulation of the dissolved cellulose through the addition of a precipitating agent,
- c) optional alkalisation of the amorphous cellulose obtained from step b),
- d) derivatisation of the amorphous cellulose obtained in step b) or c), optionally in the presence of an appropriate solvent.

Cellulose derivatives are understood to include conversion products of cellulose with appropriate derivatisation reagents such as cellulose ester (e.g. cellulose acetates, cellulose lactates, cellulose nitrates), cellulose ether ester, cellulose carbamate and especially water soluble and/or organo-soluble cellulose ethers such as carboxyalkyl celluloses (e.g. carboxymethyl cellulose), hydroxyalkyl celluloses (e.g. hydroxyethyl- and hydroxypropyl celluloses), carboxyalkylhydroxyalkyl celluloses (such as carboxymethylhydroxyethyl-, carboxymethylhydroxypropyl cellulose), sulfoalkyl cellulose derivatives (e.g. sulfoethyl cellulose, sulfopropyl cellulose, methyl sulfoethyl cellulose, methyl sulfopropyl cellulose, carboxymethyl sulfoethyl cellulose, carboxy methyl sulfopropyl cellulose, hydroxyethyl-

5 /hydroxypropylsufopropyl-cellulose ether), alkyl celluloses (e.g. methyl cellulose, ethyl cellulose), alkyl hydroxyalkyl celluloses (e.g. methyl hydroxyethyl cellulose, ethylhydroxyethyl cellulose, methylhydroxypropyl cellulose, ethylhydroxypropyl cellulose), alkylene celluloses (e.g. allyl cellulose), alkylene alkyl celluloses (e.g. allylmethyl cellulose, allylethyl cellulose), dialkyl aminoalkyl celluloses (e.g. diethyl aminoethyl cellulose), dialkylaminoalkylhydroxyalkyl celluloses (e.g. diethylaminoethylhydroxyethyl cellulose) and binary or tertiary ionic or non-ionic cellulose ethers from the above-named functional groups.

10 The derivatisation preferably takes place in the presence of the precipitating agent used for coagulation of the dissolved cellulose. Suitable precipitating agents are organic solvents such as 2-propanol, 2-methyl-2-propanol, acetonitrile, acetone, dimethylether, dioxane, methyl chloride, ethyl chloride (etherification, carbamination), and methylene chloride, glacial acetic acid, carboxylic acid
15 anhydrides such as acetic acid, propionic acid and butyric acid anhydrides (esterification) and mixtures of these solvents.

The process for derivatisation of the cellulose according to the invention is preferably implemented as follows:

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- a) cellulose is dissolved in the aminoxide/water system with the addition of stabilisers,
 - b) the dissolved cellulose is precipitated out by the addition of organic solvents
25 and attached aminoxide is removed by washing with the solvent used for sedimentation, and
 - d) the amorphous cellulose obtained in the above manner is converted in the presence of the organic solvent used for the coagulation, whereby step c)
30 (alkalisation) is omitted.

The present invention also provides the cellulose derivatives produced in accordance with the derivatisation process of the invention.

5 The cellulose derivatives according to the invention exhibit improved solubility and are largely free from fibre and gel particles. Even those cellulose derivatives according to the invention with low degrees of substitution still exhibit an excellent solubility in water and/or organic solvents.

10 The activation of cellulose according to the invention and the subsequent conversion to cellulose derivatives will be described in greater detail with reference to the following examples.

Exemplary embodiments**Example 1**5 **Activation of cellulose**

53 g cellulose (cellulose, DP_{Cuoxam} 580, water content 5.7%) were suspended with the addition of 0.75 g gallic acid propyl ester in 2800 g of a 46% aqueous N-methylmorpholine-N-oxide solution (NMMNO). At a temperature of 105°C and
10 60-65 mbar pressure, 1320 g water were distilled off, thereby dissolving the cellulose. At 85°C, 1500 ml 2-propanol were added to the cellulose solution with stirring. The cellulose sediment was filtered off, washed free of NMMNO with 2-propanol and adjusted in a filter centrifuge to a dry content of approximately 10%.

15 In the X-ray investigation of the activated cellulose (DP_{Cuoxam} 550), the crystalline parts of the starting material could no longer be detected. The water retaining value (WRV) of the activated cellulose was $3.30 \text{ cm}^3\text{g}^{-1}$. By comparison, the non-activated starting cellulose had a WRV value of only $0.65 \text{ cm}^3\text{g}^{-1}$.

20 When using cotton linters (DP_{Cuoxam} 640, $WRV=0.60 \text{ cm}^3\text{g}^{-1}$), the water retaining value of the correspondingly activated material was $3.37 \text{ cm}^3\text{g}^{-1}$ (DP_{Cuoxam} 560).

The activated celluloses used were soaked with 2-propanol for the subsequent conversions.

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Example 2

Hydroxyethyl cellulose

The activated cellulose (made from linters, $DP_{\text{Cuoxam}} 560$) soaked in 2-propanol, was suspended under a nitrogen atmosphere in a 1:1 mixture (w/w) of 2-propanol and 2-methyl-2-propanol (7.5 wt. % cellulose in the suspension mixture), and at 10°C, 0.8 mol sodium hydroxide/mol anhydro-glucose unit (AGU) of the cellulose and 5 mol water/mol AGU were added. After stirring for 160 minutes at this temperature, 2 mol ethylene oxide/mol AGU were added by metered doses and the reaction mixture was tempered for 80 minutes at 25°C. The reaction mixture was then stirred further for 100 minutes at 75°C. After cooling to room temperature, the remaining ethylene oxide was removed under vacuum, ventilated with nitrogen and the reaction mixture was neutralised with acetic acid. The reaction product was filtered off, washed free of salt with methanol and dried in the vacuum. The hydroxyethyl cellulose obtained exhibited a molar substitution level of $MS=1.34$ (equivalent to a reagent yield of ethylene oxide of 67%) and contained 7% water-insoluble matter.

When non-activated cellulose (Linters, $DP_{\text{Cuoxam}} 640$) was used under the same reaction conditions, a hydroxyethyl cellulose with $MS=0.33$ and a reagent yield of ethylene oxide of 17% was obtained; the aqueous solution contained 81% insoluble fibre and gel particles.

Example 3

Sulfoethyl cellulose

Activated cellulose (made from cellulose, $DP_{\text{Cuoxam}} 1120$, dry content 10%) soaked in 2-propanol was suspended with a bath ratio of 1:22 in a mixture of 88.6 vol.% 2-propanol, 4.4 vol.% methanol and 7.0 vol.% water. After addition of 2.4 mol sodium hydroxide/mol AGU, alkalisation was carried out for 80 minutes at 20°C under nitrogen. Then 0.8 mol sodium vinyl sulfonate/mol AGU in the form of 30% aqueous solution were added. Over a period 30 minutes, the reaction mixture was

heated to 70°C and then stirred for 120 minutes at this temperature. After cooling to room temperature, the reaction mixture was neutralised with acetic acid and filtered off. The reaction product was washed free of salt with 70% aqueous methanol and dried at 60°C in an ambient-air drying cabinet. The sulfoethyl cellulose obtained in this manner exhibited a level of substitution of DS=0.19 with a reaction yield of sodium vinyl sulfonate of 24%. The 2% aqueous solution had a viscosity of $\eta=32000$ mPas with a shear gradient of $D=2.55$ s⁻¹.

When non-activated cellulose (DP_{Cuoxam}1620) was used, a sulfoethyl cellulose with DS=0.23 was obtained with a reagent yield of 29%; the 2% aqueous solution contained fibres and gel particles.

Example 4

15 Carboxymethyl cellulose

90 g activated cellulose (containing 36 mmol cellulose) soaked in 2-propanol with a DP_{Cuoxam}830 were suspended in a 250 ml stirring vessel in a mixture of 98.4 ml 2-propanol, 14.7 ml ethanol and 22.8 ml water. At room temperature and under the exclusion of oxygen, 2.6 mol sodium hydroxide/mol AGU of the cellulose were added and stirred for 80 minutes. After the addition of 1.3 mol monochloroacetic acid/mol AGU (in 80% aqueous solution), the reaction mixture was heated to 70°C, stirred for 120 minutes at this temperature and cooled to room temperature. The reaction product was filtered off, washed with 80% aqueous ethanol until neutral and free from chloride, and then dried. The degree of substitution of the carboxymethyl cellulose, which formed a clear solution in water, was DS=0.92, corresponding to a reagent yield of monochloroacetic acid of 71%.

When non-activated cellulose was used, a carboxymethyl cellulose with $DS=0.76$ was obtained with a reagent yield of 58.5%; the 2% aqueous solution contained fibres and gel particles.

5 Example 5

Methyl cellulose

Activated cellulose (made from cellulose $DP_{Cuoxam}1270$) soaked in 2-propanol, was
10 suspended under a nitrogen atmosphere with a bath ratio of 1:20 in a mixture of 2-
propanol, methanol and water in the proportions 18:1:1.5. After the addition of
11 mol sodium hydroxide/mol AGU of the cellulose, the reaction mixture was
stirred for 90 minutes at 25°C. Then, 10 mol methyl chloride/mol AGU was added
in metered doses, the reaction mixture was heated over a period of 30 minutes to
15 85°C and stirred for 120 minutes at this temperature. After cooling to room
temperature, the pressure was reduced to normal pressure and the volatile fractions
were removed in the vacuum. The remaining dry residue was placed into boiling
water, neutralised with glacial acetic acid and washed in hot water until salt free.
The reaction mixture was filtered while still hot and the residue was dried in the
20 ambient-air drying cabinet. The methyl cellulose obtained had a level of substitution
of $DS=1.38$ with 5% water-insoluble particles.

When non-activated cellulose ($DP_{Cuoxam}1620$) was used under the same reaction
conditions, a methyl cellulose with $DS=1.17$ and 57% water-insoluble particles was
25 obtained.

Example 6

Cellulose lactate

27.2 g activated cellulose (made from linters, DPC_{uoxam}560) soaked in 2-propanol, dry content 18.35% equivalent to 31 mmol AGU) were suspended at room temperature in 150 ml dimethyl acetamide. The 2-propanol present in the mixture was distilled off quantitatively in the vacuum while stirring. After addition of 4 mol
5 L-lactide (L-3,6-dimethyl-1,4-dioxane-2,5-dione)/mol AGU of the cellulose, the reaction mixture was heated to 130°C and stirred for 5 h at this temperature. Then the reaction mixture was cooled to room temperature, 500 ml water were added and the mixture was filtered off. The residue was washed twice in each case with 500 ml of a mixture of water and acetone (3:1, v/v) and dried at 55°C in the ambient-air
10 drying cabinet. The NMR-spectroscopically determined molar degree of substitution of the cellulose lactate obtained was MS=1.8. The softening point of the product is approximately 230°C (Kofler bench).

When the native starting material (linters) is used, no reaction takes place. In
15 accordance with NMR spectroscopy, the isolated material is an unchanged cellulose I-modification.